



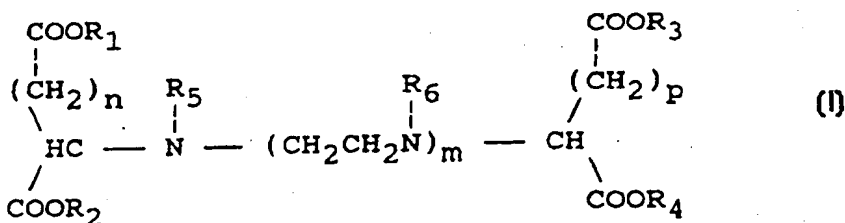
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(21) International Application Number: PCT/FI97/00106 (22) International Filing Date: 19 February 1997 (19.02.97) (30) Priority Data: 960756 19 February 1996 (19.02.96) FI (71) Applicant (for all designated States except US): KEMIRA CHEMICALS OY [FI/FI]; P.O. Box 330, FIN-00101 Helsinki (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): RENVALL, Ilkka [FI/FI]; Purovarsi 4 B, FIN-02300 Espoo (FI). AKSELA, Reijo [FI/FI]; Soukan Rantatie 8 C 27, FIN-02360 Espoo (FI). PAREN, Aarto [FI/FI]; Eerolantie 1 E 16, FIN-37630 Valkeakoski (FI). (74) Agent: BERGGREN OY AB; P.O. Box 16, FIN-00101 Helsinki (FI).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments. In English translation (filed in Finnish).</i>	

(54) Title: PROCESS FOR THE TREATMENT OF CHEMICAL PULP

(57) Abstract

A process for the bleaching or delignification of chemical pulp, wherein, before bleaching or delignification with an oxygen chemical, the pulp is pretreated with a chelating agent in order to eliminate the adverse effects of any heavy metals present in the pulp. The chelating agent used consists of compounds according to Formula (I), where n is 1-3, m is 0-3, p is 1-3, R₁, R₂, R₃ and R₄ are H, Na, K, Ca or Mg, R₅ and R₆ are H, CH₂OH, CH₂CH₂OH or CH₂O(CH₂CH₂O)₁₋₁₀CH₂CH₂OH.



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Process for the treatment of chemical pulp

The invention relates to a process for the bleaching or delignification of pulp, wherein, before bleaching or delignification with an oxygen chemical, the pulp is pretreated with a chelating agent in order to eliminate the adverse effects of any heavy metals present in the pulp.

Ever more commonly, bleaching processes using no elementary chlorine or chlorine compounds are used for the bleaching of chemical pulp. The first-mentioned bleaching is called ECF (elementary chlorine free) bleaching and bleaching which is entirely free of chlorine is called TCF (total chlorine free) bleaching. Especially TCF bleaching is usually preceded by oxygen delignification. After oxygen delignification the pulp can be bleached with chlorine-free chemicals such as ozone or hydrogen peroxide in acid or alkaline solutions in pressure-free or pressurized conditions. Usable bleaching processes also include bleaching with peroxy compounds (such as peracetic acid, caron acid, or mixtures of peracids), a peroxide-enhanced oxygen step, and a peroxide-enhanced oxygen-alkali step.

Such bleaching steps are most commonly preceded by the binding of heavy metals. The metals can be removed by an acid wash. This is often disadvantageous, since at least some of the subsequent bleaching steps are carried out in alkaline conditions. If heavy metals are removed at a low pH, it is necessary first to use an acid in order to reach a low pH and in the next step an alkali to neutralize the acid. Furthermore, the acid wash removes Mg and Ca ions, which are regarded as advantageous for bleaching. The acid wash may also reduce the strength of the pulp.

Peroxy compounds such as peracetic acid and hydrogen peroxide are highly susceptible to the catalytic action of heavy metals.

The applicant's WO application publications 95/35406, 95/35407 and 95/35408 describe transition-metal activated bleaching with peroxy compounds in acid conditions. The success of the bleaching presupposes the binding of heavy metals before the bleaching and/or during the bleaching.

In the bleaching with peroxy compounds, heavy metals are bound by using agents which chelate metal ions, for example poly-aminocarboxylic acids. These include in particular ethylene diamine tetra-acetic acid and its salts (EDTA) and diethylene triamine penta-acetic acid and its salts (DTPA). The ions the most detrimental in terms of bleaching are manganese (Mn), iron (Fe) and copper (Cu). Also other heavy metals, such as chromium ions (Cr), etc., have a detrimental effect, both on the consumption of peroxy compounds and often on the bleaching result, by reducing, for example, the viscosity of the bleached pulp. Detrimental heavy metals originate in the pulp, the treatment waters and the pulp-treatment apparatus.

In the bleaching of chemical pulp it is usually not possible to carry out chelating in alkaline conditions, because in such a case iron will precipitate in the form of hydroxides, oxides and oxyhydroxides, which strongly catalyze the breaking down of peroxide compounds. For this reason, the chelating preceding peroxide bleaching is carried out in acid conditions. Especially the removal of manganese has proved to be important in this case, since it does not form as stable complexes as does iron and since especially a chemical pulp often contains large amounts of manganese. In publication P.S. Bryant and L.L. Edwards, Tappi Pulping Conference 1993, pp. 43-55, "Manganese removal in closed kraft mill bleach plants" it is noted that manganese can best be removed at a pH of 4.5-6.5, before the manganese becomes too strongly bound to the pulp.

In modern processes for the bleaching of chemical pulp, the

bleaching is preceded by oxygen delignification. In this process there are added to the pulp magnesium ions, the remaining of which in the pulp is important in a bleaching with peroxide compounds, for example hydrogen peroxide. According to the article, the best Mg/Mn ratio is reached at a pH of 4.5-5.0. For this reason the chelating should in practice be carried at a pH clearly below 6, for example at a pH close to 5.5. In the examples of the above reference publication, the chelating was carried out at a pH of 5.3.

Effective chelating agents are often poorly biodegradable, as is DTPA, or are completely non-biodegradable, as is EDTA. The increasing of TCF bleaching has increased the use of the said chelating agents. Therefore interest has arisen in replacing poorly biodegradable chelating agents either in part or entirely with biodegradable chelating agents. In order to avoid the environmental load it is additionally desirable that the biodegradable chelating agents be preferably phosphorus-free and also contain as small an amount of nitrogen as possible.

Biodegradable complexing agents have been developed for detergent builders. They must at the same time have softening action on water, i.e. they must bind calcium ions and magnesium ions. One such sequestering agent is ethylenediamine disuccinic acid (EDDS). This compound has three stereoisomers.

The substance is known per se from F. Pavelcek's and J. Majer's publication "New Complexanes. XXXIV. Preparation and properties of the meso and rac forms of ethylenediamine-N,N'-disuccinic acid," Chem. Zvesti 32 (1978), pages 37-41. FI Patent 86554 of Procter & Gamble discloses the use of this substance in detergent compositions. Application publication WO 94/03553 of the same applicants discloses the use of the substance in bleaching liquors as a stabilizer of peroxy compounds in the bleaching of pulp and in detergents. The more detailed description and examples relate only to the latter. In this case the pH of the

bleaching liquor must be 0.5-6.0. The publication mentions that the compound is biodegradable. According to the patent, the S,S-isomer of EDDS is the best biodegradable.

EP patent application 556 782 discloses the use of EDDS as an iron complexer in photography chemicals. Example 9 of the publication mentions that the ferric salts of EDTA, DTPA and HEDTA are not biodegradable. In contrast, the Fe^{2+} salt of EDDS is biodegradable. The biodegradabilities of the compounds were tested in the example by a generally approved testing method (301C Amendment MITI Test (I), OECD Chemical Substance Testing Guidelines, May 1981).

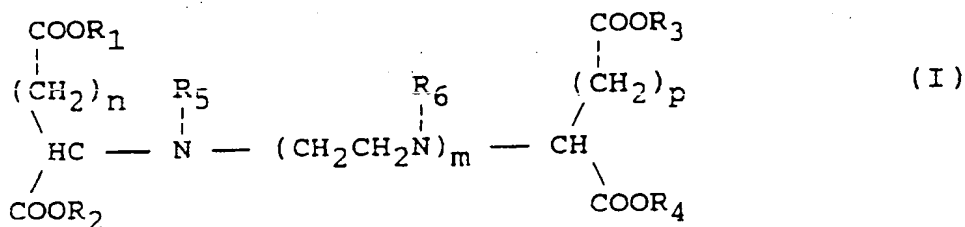
Another known biodegradable complexing agent is 2,2'-imino-disuccinic acid (ISA). The use of this compound in alkaline detergents is disclosed in EP patent application 509 382. The patent application mentions the use of 2,2'-iminodisuccinic acid as a stabilizer of peroxide compounds, in particular in alkaline detergent compositions which contain hydrogen peroxide and its derivatives. In the examples of the application, only perborate is used. Since perborate releases hydrogen peroxide only slowly, no far-reaching conclusions can be drawn from the examples of the patent regarding the stabilization of hydrogen peroxide in similar detergent compositions.

DE patent application 4 216 363 discloses the use of ISA as a stabilizer of tensides. There is no mention of the use of a peroxide compound. EP patent application 513 948 mentions the use of the substance in detergents which are intended for hard surfaces and contain an organic solvent boiling at approx. 90 °C. There is no mention of the use of a peroxide compound.

DE patent application 4 340 043 discloses the use of ISA as a bleaching agent in the bleaching of groundwood pulp. According to the publication, the purpose of ISA is the stabilization of hydrogen peroxide, and the examples show that at a pH of 10 it

The object of the present invention is to eliminate the adverse effects of heavy metals in the bleaching and delignification of chemical pulp. It is also an object to obtain a biodegradable effective chelating agent which yields a good bleaching result.

In the process according to the invention, compounds according to Formula I, known per se, are used.


$$\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{1-10}\text{CH}_2\text{CH}_2\text{OH}.$$

It has now been observed, surprisingly, that compounds according to Formula I can be used advantageously, at a higher pH than can DTPA, as chelating agents in a pretreatment step preceding the bleaching or delignification of pulp. Suitable pH

values in the use of the compounds in accordance with the invention for the pretreatment of pulp are pH 4-8, preferably pH 5.0-7.5 and most preferably pH 6.5-7.5. If the compounds are also used in the actual bleaching or delignification step, the suitable pH values are respectively pH 4-8, preferably pH 4-6 and most preferably pH 4-5. Since chelating can be carried out at a higher pH value, the consumption of alkali in the subsequent step is not as high as when the chelating is carried out at a lower pH. This is a clear advantage over, for example, DTPA.

The process according to the invention can be used for all known chemical pulps. These include alkaline and neutral sulfite pulps, soda pulps, sulfate pulps (kraft pulps) and oxygen-delignified (oxygen cooking) sulfate pulps. Furthermore, the process can be used in the bleaching of so-called organosolv pulps in which alcohols or organic acids have been used as the cooking solvent, for example Milox cooking in formic acid. The chelating process according to the invention may also be used when polysulfides or, for example, anthraquinone, have/has been used in sulfate cooking.

The treatment can be carried out on pulp cooked from different fiber raw materials, such as softwood, hardwood or reed, straw or other raw material of vegetable origin.

The chelating process according to the invention with compounds of Formula I, e.g. EDDS and ISA, is used as a pretreatment before bleaching or delignification with oxygen chemicals. Chelating agents according to Formula I, such as EDDS and ISA, can also be used as a chelating agent in bleaching or delignification with oxygen chemicals. These include bleaching with peracetic acid, bleaching with mixtures of peracids, bleaching with hydrogen peroxide, bleaching with mixtures of hydrogen peroxide and peracids, transition-metal catalyzed hydrogen peroxide bleaching within the acid pH range, developed by the

applicant, alkaline peroxide bleaching, and combinations of all these, as well as oxygen delignification, peroxide-enhanced oxygen-alkali steps and pressurized peroxide steps and, in conjunction with these, optional treatments with enzymes, ozone or chlorine dioxide.

The chelating process according to the invention can be used as a pretreatment for pulp bleaching or delignification in acid conditions and possibly also in the bleaching or delignification step itself.

The pH control of an acid chelating step can be carried out using conventional mineral acids, such as sulfuric acid, sulfur dioxide or an aqueous solution thereof, carbon dioxide, or organic acids such as formic acid and acetic acid.

In the process according to the invention, an especially suitable chelating agent according to Formula I may be ethylenediamine-N,N'-disuccinic acid, its various isomers and its alkali metal salts, such as sodium and potassium salts, and its earth-alkali metal salts, such as calcium and magnesium salts. It is also possible to use ethylenediamine-N,N'-disuccinic acid together with calcium sulfate and/or magnesium sulfate. Another particularly suitable chelating agent is 2,2'-iminodisuccinic acid, its various isomers and its alkali metal salts, such as sodium and potassium salts, and its earth-alkali metal salts, such as calcium and magnesium salts. It is also possible to use 2,2'-iminodisuccinic acid together with calcium sulfate and/or magnesium sulfate.

Usable chelating agents also include N-(1,2-dicarboxyethyl)-N-(2-hydroxyethyl)aspartamic acid, its various isomers and its alkali metal salts and earth-alkali metal salts. The acid may also be used together with potassium sulfate or magnesium sulfate.

The chelating agent may be added in an amount of 0.1-5 kg, preferably 0.5-2 kg per metric ton of dry pulp.

It has also been observed that EDDS and ISA can be used together with hydroxycarboxylic acids without the bleaching result being worsened. EDDS and ISA may in part be replaced with chelating agents which do not contain nitrogen, such as hydroxycarboxylic acids having the general formula II



where

n is 1-8,

m is 0-2n,

p is 0-n,

q is 0-2,

R₁ is COOH, and

R₂ is H, CH₂OH or COOH.

The detrimental nitrogen load in effluents from bleaching can thus be reduced. Conventional carboxylic acids, hydroxycarboxylic acids, polyhydroxycarboxylic acids and hydroxypoly-carboxylic acids according to Formula II, such as citric acid, tartaric acid, lactic acid, pimelic acid, glutamic acid, glucoheptonic acid, ascorbic acid, glycolic acid, glutaric acid, adipic acid, succinic acid or malonic acid, can be used as replacement chelating agents.

It is quite surprising that hydroxy acids can be used as chelating agents in bleaching. The said substances are quite poor binders of heavy metals, but bind well calcium and magnesium. Especially citric acid has been used as a replacement for phosphates in phosphate-free detergents and cleansing agents, in which the substances are required to bind calcium and magnesium. Especially the binding of magnesium should be disadvantageous in terms of bleaching.

The invention is illustrated below with examples, which do not, however, limit the invention to relate only to the examples presented here.

The following acronyms are used in the examples: CS stands for consistency, PAA for a peracetic acid treatment, mP for a molybdate-activated peroxide treatment, O for an oxygen treatment, P for an alkaline peroxide treatment, and Q for a chelating step. The doses in the tables are indicated in kilograms per metric ton of pulp (kg/tp).

Example 1

To investigate the chelating of heavy metals and earth alkali metals, an oxygen-delignified chemical pulp was washed with aqueous solutions containing EDDS. The metal contents of the washing solution were analyzed after the wash. Thereby the transfer of iron (Fe), manganese (Mn), calcium (Ca) and magnesium (Mg) into the washing waters was investigated. The transfer of iron and manganese into the washing solutions is advantageous for bleaching. In contrast, the transfer of calcium and magnesium into the washing solutions is disadvantageous for bleaching. In the reference tests the pulp was washed with DTPA or EDTA solutions. The chelating agent concentrations and the pH during the wash are indicated in Table 1.

Table 1

Softwood sulfate pulp		Chelating conditions	
Kappa number	16.9	Time (t)	60 min
Viscosity	963 dm ³ /kg	Temperature (T)	70 °C
Brightness	39.6 % ISO	Consistency (CS)	12 %

Chelate	Dose kg/tp	pH	Metal contents in the filtrate (ppm)			
			Fe	Mn	Mg	Ca
Na ₅ DTPA	1	6.7	1.2	2.9	4	17
Na ₅ DTPA	2	5.7	2.0	3.3	13	52
Na ₅ DTPA	2	6.5	2.0	2.8	17	48
Na ₄ EDTA	2	6.5	1.8	3.3	5	49
H ₄ EDDS	1	5.9	2.0	2.0	12	45
H ₄ EDDS	1	6.8	1.6	2.6	7	15
H ₄ EDDS (reaction mixture)	1.5	5.5	2.0	1.5	15	55
H ₄ EDDS (reaction mixture)	1.5	6.5	1.9	2.3	13	37
H ₄ EDDS (S,S)	2	5.0	2.0	1.6	15	35
H ₄ EDD (S,S)	2	6.8	2.0	3.0	17	36
H ₄ EDDS (R,R + R,S)	2	5.5	1.9	1.8	13	50
H ₄ EDDS (R,R + R,S)	2	6.5	1.7	3.3	18	30

In Table 1, Na₅DTPA stands for the pentasodium salt of DTPA, Na₄EDTA stands for the tetrasodium salt of EDTA, and H₄EDDS stands for the acid form of EDDS. However, the pH used will determine how the chelating agents are dissociated, i.e. in which form they actually appear in the treatment. The H₄EDDS (reaction mixture) mentioned in the table refers to experiments in which the chelating agent used was an unpurified reaction product directly from the process for the preparation of EDDS.

It was observed in the experiments that, when EDDS was used at a rate of 1.5 kg/metric ton of pulp, the chelating of iron and manganese was nearly as complete as when EDTA or DTPA was used at a rate of 2.0 kg/tp in the same experimental conditions. At a lower pH the chelating of manganese was not as complete as when the reference substances were used, but at a pH of 6.5 and

in more alkaline conditions manganese was chelated as well as or better than when the reference substances were used. EDDS chelated calcium and magnesium less than did the reference substances, which is advantageous in terms of bleaching.

No significant differences were observed in the experiments in the chelating properties among the S,S isomer of EDDS, a mixture R,R and R,S isomers of EDDS, and a chelating agent containing all isomers of EDDS.

Example 2

Table 2 shows the results of washing experiments similar to those described in Example 1, when EDDS was diluted with certain hydroxy acids.

Table 2

Softwood sulfate pulp		Chelating conditions	
Kappa number	16.9	Time (t)	60 min
Viscosity	963 dm ³ /kg	Temperature (T)	70 °C
Brightness	39.6 % ISO	Consistency (CS)	12 %

Chelate	Dose kg/tp	pH	Metal contents in the filtrate (ppm)			
			Fe	Mn	Mg	Ca
Na ₅ DTPA	1	6.7	1.2	2.9	4	17
Na ₅ DTPA	2	6.5	2.0	2.8	17	48
Na ₅ DTPA	2	5.7	2.0	3.3	13	52
Na ₅ DTPA	0.5	6.6	0.8	1.5	5	26
Na ₄ EDTA	2	6.5	1.8	3.3	5	49
Water wash		6.0	0.3	0.3	6	22
Water wash		7.0	0.3	0.3	14	66
Na ₃ citrate	1	6.3	0.0	0.6	9	26
H ₄ EDDS + Na ₃ citrate	0.5+1	7.5	1.3	2.4	8	18
H ₄ EDDS + Na ₃ citrate	0.75+1	5.7	2.2	1.6	17	58
H ₄ EDDS + Na ₃ citrate	1+1	7.4	1.4	2.7	10	23
H ₄ EDDS	1.5	7.1	1.9	2.3	13	37
H ₄ EDDS + Na gluconate	1+1	6.7	1.8	2.6	9	29
H ₄ EDDS + Na gluconate	1+1	8.9	0.3	2.2	10	5

In the chelating step, DTPA is usually dosed into a softwood pulp at a rate of approx. 2 kg/tp. In the second series of experiments (Table 2), the effect of the DTPA dose on the chelating of metals was first investigated. Chelating was clearly less when the dose of EDDS was reduced from a rate of 2.0 kg/tp to a rate of 1.0 kg/tp or 0.5 kg/tp. In the previous series of experiments (Table 1) it was observed that when Na₄EDDS was used at a rate of 1.5 kg/tp, chelating was as complete as when Na₅DTPA was used at a rate of 2.0 kg/tp.

Practical experience and the above results of experiments indicate that DTPA must be used in the chelating step at a rate of approx. 2.0 kg/tp and EDDS at a rate of approx. 1.5 kg/tp in

order for the heavy metals to be chelated sufficiently completely for bleaching. When sodium salts of citric acid or gluconic acid were used as a chelating agent alongside EDDS, it was possible to reduce the dose of EDDS significantly. Even though the dose of EDDS had been lowered to a rate of 1.0 kg/tp, the chelating of metals in these experiments was as complete as when EDDS was used at a rate of 1.5 kg/tp. By the use of, for example, salts of hydroxycarboxylic acids together with EDDS as the chelating agent, the nitrogen load in the effluents from the chelating step can be reduced significantly, while the chelating of the metals is still sufficiently complete for bleaching.

It can be observed from Table 2 that a water wash has no effect as regards the chelating of metals. Likewise, citric acid used alone does not remove heavy metals. Citric acid chelates only earth-alkali metals, which is not desirable for bleaching. This indicates that a good chelating result is achieved through the joint effect of EDDS and, for example, citric acid.

It is to be noted that a conclusion regarding the bleaching result cannot be drawn directly from washing experiments such as described above. For this reason the effect of corresponding chelating steps on alkaline hydrogen peroxide bleaching was investigated.

Example 3

An oxygen-delignified pulp was chelated and bleached with an alkaline hydrogen peroxide. The chelating agent used was EDDS or DTPA. The results are compiled in Table 3. The bleaching result can be evaluated on the basis of the consumption of peroxide, the brightness achieved, and the viscosity of the pulp.

Table 3

Pretreatment: -O-mP-P-

Kappa 5.2
 Viscosity 817 dm³/kg
 Brightness 74.7 % ISO

Q

No.	1	2	3	4	5	6	7	8	9
t, min	60	60	60	60	60	60	60	60	60
T, C	75	75	75	75	75	75	75	75	75
CS, %	12	12	12	12	12	12	12	12	12
pH	5	6.5	5	6.5	5.0	6.5	6.5	6.5	6.5
Na ₅ DTPA, kg/tp	2	2	1	-	1.5	1.5	3	1.5	0.6
Na ₄ EDDS, kg/tp				-				MgSO ₄	
Other kg/tp				-				1	

P

t, min	180	180	180	180	180	180	180	180	180
T, C	90	90	90	90	90	90	90	90	90
CS, %	12	12	12	12	12	12	12	12	12
pH, initial	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4
pH, final	10.3	10.2	10.1	10.3	10.1	10.1	10.4	10.2	10.2
H ₂ O ₂ , kg/tp	20	20	20	20	20	20	20	20	20
Residual H ₂ O ₂ , kg/tp	17.5	14.4	8.2	3	6.2	13.7	15.1	15.6	15.9
Residual H ₂ O ₂ , %	87.5	72	41	15	31	68.5	75.5	78	79.5
Residual NaOH, kg/tp	7.1	6.8	4.8	4.3	4.5	6.4	7.1	7	7.4
Kappa	3.9	3.7	3.6	3.5	3.5	3.7	3.7	3.8	3.7
Viscosity	787	736	606	575	603	791	752	755	792
Brightness, % ISO	83.9	85.1	84.9	86	84.8	85.3	85.3	84.8	85.1
H ₂ O ₂ consumption, kg/tp	2.5	5.6	11.8	17.0	13.8	6.3	4.9	4.4	4.1

In a reference experiment the chelating was carried out with DTPA before bleaching (Experiment 1). When the chelating with EDDS was carried out at a pH of 5.5, the bleaching result was poor (Experiment 5). In contrast, when the chelating with EDDS was carried out at a pH of 6.6 (Experiment 6), the bleaching result was better than in the reference experiment (Experiment 2).

It is to be noted that, in the reference experiments, appropriate bleaching results were obtained only when DTPA was used in the chelating at a rate of at minimum 2 kg/metric ton of pulp (Ref. Experiment 3). In contrast, when the chelating was carried out by using EDDS at a rate of only 0.6 kg/tp, a good bleaching result was obtained (Experiment 9). This means a considerable reduction in the consumption of chemicals in bleaching. The use of magnesium sulfate as an additive in chelating, alongside EDDS, is also advantageous in terms of bleaching (Experiment 8).

Example 4

In this experiment, the effect of EDDS and the salts of hydroxycarboxylic acids on chelating was investigated. Pre-treated softwood pulp described in Example 3 was used in the experiment. The chelating of the pulp and the alkaline peroxide bleaching were carried out in conditions described in Table 4.

Table 4

Kappa 5.2
 Viscosity 817 dm³/kg
 Brightness 74.7 % ISO

Q		1	2	3	4	5	6	7	8	9
No.										
t, min		60	60	60	60	60	60	60	60	60
T, °C		75	75	75	75	75	75	75	75	75
CS, %		12	12	12	12	12	12	12	12	12
pH		5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Na ₅ DTPA, kg/tp		2	1.5	0.6	0.3	1	0.6	0.6	0.3	
Na ₄ EDDS, kg/tp				0.5	0.5	1				
Na gluconate kg/tp							0.8	0.4	0.4	1
Na citrate kg/tp										
P										
t, min		180	180	180	180	180	180	180	180	180
T, °C		90	90	90	90	90	90	90	90	90
CS, %		12	12	12	12	12	12	12	12	12
pH, initial		10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4
pH, final		10.3	10.1	10.3	10.3	10.2	10.2	10.3	10.3	10.3
H ₂ O ₂ , kg/tp		20	20	20	20	20	20	20	20	20
Residual H ₂ O ₂ , kg/tp		17.5	13.7	12.7	12.3	14.4	15	14.7	13.2	3.7
Residual H ₂ O ₂ , %		87.5	68.5	63.5	61.5	72	75	73.5	66	18.5
Residual NaOH, kg/tp		7.1	6.4	6.4	6.1	6.8	7.1	7.1	7.2	5
Kappa		3.9	3.7	3.6	3.5	3.5	3.7	3.7	3.7	3.5
viscosity dm ³ /kg		787	791	738	750	756	767	782	755	572
Brightness, % ISO		83.9	85.3	85.7	85.7	85.4	85.7	85.8	85.2	85.4
H ₂ O ₂ consumption, kg/tp		2.5	6.3	7.3	7.7	5.6	5.0	5.3	6.8	16.3

In the reference experiments the chelating was carried out with DTPA and EDDS. When sodium citrate alone was used in the chelating step, the bleaching result was poor (Experiment 9). In contrast, in experiments in which sodium gluconate or Na citrate was used together with EDDS in the chelating, the bleaching results were good.

When biodegradable auxiliary agents which did not contain nitrogen, such as Na gluconate or Na citrate, were used together with EDDS in the chelating, the dose of EDDS could be reduced even down to a rate of 0.25 kg/tp without the bleaching result being worsened. This is a significant result, for example in terms of the treatment of effluents. By the use of chelating agent mixtures described above, the nitrogen load in the effluents from bleaching can be reduced significantly.

Example 5

As a reference experiment, chelating and an alkaline peroxide bleaching were carried out on a softwood pulp which had been delignified with peracetic acid after oxygen delignification. The conditions of the chelating and the bleaching are described in Table 5. In the reference experiments the chelating was carried out with DTPA.

Table 5

Softwood sulfate pulp

Initial treatment:

-O-PAA-

Kappa

5.3

Viscosity

777 dm³/kg

Brightness

65.7 % ISO

Q

No.	1	2	3	4	5
t, min	60	60	60	60	
T, C	75	75	75	75	
CS, %	12	12	12	12	
pH	5	6.6	5.1	6.4	
Na ₅ DTPA, kg/ts	2	2			
Na ₄ EDDS, kg/ts			1.5	1.5	

P

	↓	↓	↓	↓	No chelating
t, min	180	180	180	180	180
T, C	90	90	90	90	90
CS, %	12	12	12	12	12
pH, initial	10.4	10.4	10.4	10.4	10.4
pH, final	9.7	9.8	9.8	9.8	9.5
H ₂ O ₂ , kg/tp	20	20	20	20	20
Residual H ₂ O ₂ , kg/tp	4.1	4.1	6.1	8.2	3
Residual H ₂ O ₂ , %	20.5	20.5	30.5	41	15
Residual NaOH, kg/tp	2	2.4	2.3	2.8	1.8
Kappa	2.2	2.3	2.2	2.2	2.2
Viscosity, dm ³ /kg	535	553	565	599	465
Brightness % ISO	85.0	85.0	85.2	85.7	84.6

No chelating was performed in Experiment 5. This led to a poor bleaching result. In particular, the viscosity of the pulp was considerably reduced. After chelating steps at a pH of 5 and at a pH of 6.5, the bleaching results achieved were better in experiments in which EDDS was used than in experiments in which DTPA was used. Judged on the basis of viscosity and brightness,

the best bleaching result was achieved when the chelating step had been carried out by using EDDS at a pH of 6.4. The dissociation of hydrogen peroxide was considerably less in this experiment than in a reference experiment in which the chelating had been carried out with DTPA. It is to be noted that in these experiments, also, the amount of EDDS used (1.5 kg/tp) was considerably lower than the amount of DTPA used (2.0 kg/tp).

Example 6

In this experiment, an oxygen-delignified softwood pulp was bleached with an alkaline hydrogen peroxide by adding the chelating agent directly to the bleaching liquor. In reference experiments the chelating was carried out with DTPA or EDDS before the bleaching. The pulp used in the reference experiments was also pre-bleached with peracetic acid before the chelating. The conditions and results of the experiments are compiled in Table 6.

Table 6

Softwood sulfate pulp

Viscosity 777 dm³/kg

Kappa 6.7

Brightness 65.7 % ISO

O₂ delignification

PAA delignification

Chelating

t, min	60	60	60
T, C	75	75	75
CS, %	12	12	12
pH	6.5	6.5	6.5
Chelate	-	Na ₅ DTPA	Na ₄ EDDS
kg/tp	0	2	1.5

↓ ↓ ↓

Bleaching

t, min	180	180	180	180	180	180
T, C	90	90	90	90	90	90
CS, %	12	12	12	12	12	12
pH	10.4	10.4	10.4	10.4	10.4	10.4
H ₂ O ₂ , kg/tp	20	20	20	20	20	20
					Na ₅ DTPA 2 kg	Na ₄ EDDS 1.5 kg
Residual H ₂ O ₂ , kg/tp	2.5	11.5	13.1	8.7	10.3	10.5
Residual H ₂ O ₂ , %	12.5	57.5	65.6	43.5	51.5	52.5
Kappa	2.3	2.4	2.5	5.3	5.3	5.3
Viscosity, dm ³ /kg	449	561	582	661	676	679
Change in viscosity, %	29	11	7	7	5	4
Brightness, % ISO	88.5	88.8	88.8	84.0	83.9	84.2

It is to be noted that the pulp used in these experiments was considerably bright already after the pretreatment. When the

chelating agents were added directly to the bleaching liquor, the bleaching results were similar when DTPA was used at a rate of 2.0 kg/tp and when EDDS was used at 1.5 kg/tp. In experiments in which the chelating was carried out before the bleaching, a better pulp brightness was achieved. Judging from this, in terms of the bleaching results it is more advantageous to carry out a separate chelating than to add the chelating agents to the bleaching liquor.

When the separate chelating had been carried out with EDDS, viscosity was reduced less in the bleaching than in a reference experiment in which the separate chelating had been carried out with DTPA. The consumption of hydrogen peroxide was also smaller in bleaching after EDDS chelating.

Example 7

In this experiment, a softwood pulp was chelated and delignified in acid conditions with molybdate-activated hydrogen peroxide (mP step). In the reference experiment, DTPA was used for the chelating. The chelating was carried out at a pH of 6.0-6.5.

Table 7

Softwood sulfate pulp

Kappa 13.1

Viscosity 878 dm³/kg

Chelating

t, min	45	45	45
T, C	60	60	60
CS, %	12	12	12
Chelate	None	Na ₅ DTPA	Na ₄ EDDS
kg/tp	-	2	1.5

mP delignification

	↓	↓	↓
t, min	180	180	180
T, C	90	90	90
CS, %	12	12	12
H ₂ O ₂ , kg/tp	15	15	15
Mo, kg/tp	0.45	0.45	0.45
pH	5	5	5
Residual H ₂ O ₂ , kg/tp	2.6	5.7	6.7
Residual H ₂ O ₂ , %	17.3	38.0	44.7
Kappa	6.4	6.3	6.3
Brightness, % ISO	62.4	63.4	61.4
Viscosity, dm ³ /kg	789	825	820

The results (Table 7) show that without a pretreatment the peroxide consumption in the mP step was greater than it was for pretreated pulps. Likewise, the viscosity of the pulp after delignification was higher in the experiments in which chelating had been performed. The peroxide consumption of EDDS-chelated pulp in the mP step was smaller than that of a DTPA-chelated pulp.

Example 8

To investigate the chelating of heavy metals and earth-alkali metals, an oxygen-delignified chemical pulp was washed with

aqueous solutions containing ISA. The metal contents of the washing solution were analyzed after the wash. Thus the transfer of iron (Fe), manganese (Mn), calcium (Ca) and magnesium (Mg) into the washing waters was investigated. The transfer of iron and manganese into the washing solutions is advantageous for bleaching. In contrast, the transfer of calcium and magnesium into the washing solutions is disadvantageous for bleaching. In the reference experiments the pulp was washed with DTPA or EDTA solutions. The chelating agent concentrations and the pH during the wash are shown in Table 9.

Table 8

Softwood sulfate pulp		Chelating conditions	
Kappa number	16.9	Time	60 min
Viscosity	963 dm ³ /kg	Temperature	70 °C
Brightness	39.6 % ISO	Consistency	12 %

Chelate	Dose kg/tp	pH	Metal contents in the filtrate (ppm)			
			Fe	Mn	Mg	Ca
Na ₅ DTPA	1	6.7	1.2	2.9	4	17
Na ₅ DTPA	2	6.5	2.0	2.8	17	48
Na ₅ DTPA	2	5.7	2.0	3.3	13	52
Na ₅ DTPA	0.5	6.6	0.8	1.5	5	26
Na ₄ EDTA	2	6.5	1.8	3.3	5	49
Water wash		6.0	0.3	0.3	6	22
Water wash		7.0	0.3	0.3	14	66
Na ₃ citrate	1	6.3	0.0	0.6	9	26
ISA	1.5	5.8	1.1	1.9	2	50
ISA	1.5	8.9	0.0	1.3	25	26
ISA + Na citrate	1+1	7.7	0.5	2.2	15	26

In Table 8, Na₅DTPA stands for the pentasodium salt of DTPA, Na₄EDTA stands for the tetrasodium salt of EDTA, and ISA stands for the acid form of iminodisuccinic acid of ISA. However, it is the pH used that determines how the chelating agents are

is the pH used that determines how the chelating agents are dissociated, i.e. in which form they actually are present in the treatment.

It can be observed that in the water wash carried out as a reference experiment, iron and manganese dissolved poorly in water at both a pH of 6.0 and a pH of 7.0. In a more alkaline solution, more magnesium and calcium was dissolved in the washing water. A wash with a sodium salt of citric acid was also ineffective in removing iron and manganese. In contrast, in this experiment earth-alkali metals were removed to some degree, which is disadvantageous for bleaching. EDTA and DTPA chelated iron and manganese with approximately the same efficiency at a pH of 6.5.

ISA chelated iron and manganese well at a pH of 5.8. It is to be noted that ISA removed very little magnesium from the pulp at a pH of 5.8. This is advantageous for bleaching. Chelating in an alkaline solution at a pH of 8.9 was also very successful. It is to be noted that at this pH iron is precipitated. This explains the small iron contents in the filtrate.

Chelating with a mixture of ISA and the sodium salt of citric acid was also successful, considering that the chelating was carried out at a pH of 7.7.

It is to be noted that a conclusion regarding the bleaching result cannot be drawn directly from washing experiments of the type described above. Therefore the effect of corresponding chelating steps on an alkaline hydrogen peroxide bleaching was investigated.

Example 9

An oxygen-delignified pulp pretreated with a molybdate-catalyzed peroxide was chelated and bleached with an alkaline hydrogen peroxide. The chelating agent used was ISA or DTPA.

The results are compiled in Table 9. The bleaching result can be assessed on the basis of peroxide consumption and the achieved brightness and pulp viscosity.

Table 9

Pretreatment: -O-mP-P

Kappa 5.2
 Viscosity 817 dm³/kg
 Brightness 74.7 % ISO

Q											
No.	1	3	4	5	6	7	8	9	10	11	12
t, min	60	60	60	60	60	60	60	60	60	60	60
T, C	75	75	75	75	75	75	75	75	75	75	75
CS, %	12	12	12	12	12	12	12	12	12	12	12
pH	5	6.6	5	6.5	5	6.5	6.5	6.5	6.5	6.5	6.5
DTPA, kg/tp	2	2	1	-	3	3	1	1.5	0.5	0.25	0.3
ISA				No che-				Na cit-	Na cit-	Na cit-	Na cit-
Other				late				rate	rate	rate	rate
kg/tp								1	0.5	0.5	0.4
P											
t, min	180	180	180	180	180	180	180	180	180	180	180
T, C	90	90	90	90	90	90	90	90	90	90	90
CS, %	12	12	12	12	12	12	12	12	12	12	12
pH, initial	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4
pH, final	10.3	10.2	10.1	10.3	10.2	10.2	10.3	10.3	10.2	10.3	10.3
H ₂ O ₂ , kg/tp	20	20	20	20	20	20	20	20	20	20	20
NaOH, kg/tp	11	11	11	11	11	11	11	11	11	11	11
Residual H ₂ O ₂ , kg/tp	17.5	14.4	8.2	3	9.7	12.7	10.7	13.9	13.5	9.7	13.2
Residual H ₂ O ₂ , %	87.5	72	41	15	48.5	63.5	53.5	69.5	67.5	48.5	66
Residual NaOH, kg/tp	7.1	6.6	4.8	4.3	5.2	6.7	6.1	6.8	7.1	6.2	7.2
Kappa	3.9	3.7	3.6	3.5	3.6	3.6	3.6	3.7	3.6	3.5	3.7
Viscosity, dm ³ /kg	787	736	606	573	673	725	671	751	763	714	755
Brightness, % ISO	83.9	85.1	84.9	86	85	85.3	85.9	85.8	85.6	85.7	85.2

When a relatively ample ISA dose of 3.0 kg/metric ton of pulp was used in the chelating, the bleaching result was good as compared with the bleaching result after DTPA chelating. On the other hand, when ISA was used in very low concentrations, as low as 0.25 kg/metric ton of pulp, in chelating together with the sodium salt of citric acid, a good bleaching result was obtained. This is a significant improvement over chelating with DTPA. The nitrogen load in effluents from bleaching can be reduced significantly by using this bleaching process.

Example 10

In order to determine how ISA functions when bleaching is carried out in acid conditions, chelating was carried out as a pretreatment for an acid peroxide bleaching step. This latter step was the transition-metal catalyzed bleaching according to the applicant's previous invention.

Table 10

Softwood sulfate pulp

Kappa 13.1

Viscosity 878 dm³/kg

Chelating

t, min	45	45	45
T, C	60	60	60
CS, %	12	12	12
Chelate	None	DTPA	ISA
kg/tp	-	2	1.5

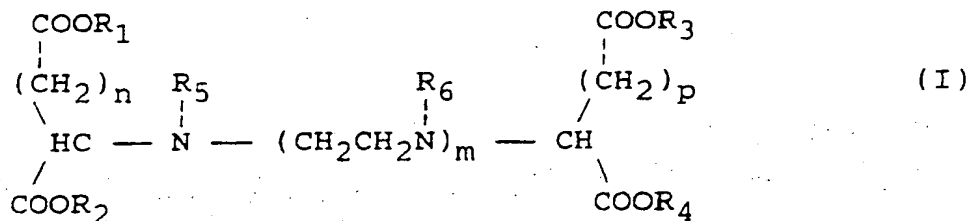
mP delignification

	↓	↓	↓
t, min	180	180	180
T, C	90	90	90
CS, %	12	12	12
H ₂ O ₂ , kg/tp	15	15	15
Mo, kg/tp	0.45	0.45	0.45
pH	5	5	5
Residual H ₂ O ₂ , kg/tp	2.6	5.7	5.2
Residual H ₂ O ₂ , %	17.3	38.0	34.7
Kappa	6.4	6.3	6.4
Brightness, % ISO	62.4	63.4	62
Viscosity, dm ³ /kg	789	825	810

The results show that without a pretreatment the consumption of peroxide in the mP step was considerably higher if no pretreatment with DTPA or ISA was performed. The viscosity of the pulp was higher if a pretreatment had been performed.

Claims

1. A process for the bleaching or delignification of a chemical pulp, in which process the pulp is pretreated, before a bleaching or delignification with an oxygen chemical, with a chelating agent in order to bind into a chelate complex the heavy metals present in the pulp, characterized in that the chelating agent used is a compound having the formula (I)



where

n is 1-3

m is 0-3

p is 1-3

R_1, R_2, R_3 and R_4 are H, Na, K, Ca or Mg

R₅ and R₆ are H, CH₂OH, CH₂CH₂OH or CH₂O(CH₂CH₂O)₁₋₁₀CH₂CH₂OH.

2. A process according to Claim 1, characterized in that the chelating agent is ethylenediamine-N,N'-disuccinic acid and/or an alkali metal salt or earth-alkali metal salt thereof.

3. A process according to Claim 1 or 2, characterized in that the chelating agent used is a sodium, calcium or magnesium salt of ethylenediamine-N,N'-disuccinic acid or ethylenediamine-N,N'-disuccinic acid and calcium sulfate and/or magnesium sulfate.

4. A process according to Claim 1, characterized in that the chelating agent used is 2,2'-iminodisuccinic acid and/or an alkali metal salt and/or earth-alkali metal salt thereof.

5. A process according to Claim 1 or 4, characterized in that the chelating agent used is a sodium, calcium or magnesium salt of 2,2'-iminodisuccinic acid or 2,2'-iminodisuccinic acid and calcium sulfate and/or magnesium sulfate.
6. A process according to Claim 1, characterized in that the pretreatment of the pulp is carried out at a pH of 4-8, preferably at a pH of 5.0-7.5 and most preferably at a pH of 6.5-7.5.
7. A process according to Claim 1 or 6, characterized in that the pretreatment with a chelating agent constitutes a step directly preceding a bleaching or delignification with an oxygen chemical.
8. A process according to any of Claims 1, 6 and 7, characterized in that the pretreatment is carried out once or several times.
9. A process according to Claim 1 or 7, characterized in that the oxygen chemical bleaching or delignification comprises bleaching with a peracetic acid, bleaching with a peracid mixture, bleaching with peroxides as such or as mixtures, either alone or as a mixture with peracids, a transition-metal catalyzed hydrogen peroxide bleaching within the acid pH range, an alkaline peroxide bleaching and combinations of all of these, as well as oxygen delignification, a peroxide-enhanced oxygen-alkali step and pressurized peroxide steps, and combined with these optional treatments with enzymes, ozone or chlorine dioxide.
10. A process according to Claim 1 or 9, characterized in that the chelating treatment is carried out also in the oxygen chemical bleaching or delignification step.

11. A process according to any of Claims 1, 9 and 10, characterized in that the oxygen chemical bleaching or delignification is carried out at a pH of 4-8, preferably at a pH of 4-6, and most preferably at a pH of 4-5.

12. A process according to any of Claims 1 and 9-11, characterized in that the oxygen chemical treatment is carried out once or several times.

13. A process according to any of Claims 1 and 9-12, characterized in that the oxygen chemical treatment of the pulp is carried out simultaneously with a peroxide and a peracid.

14. A process according to any of Claims 1 and 9-13, characterized in that the peroxide treatment of the pulp is carried out with hydrogen peroxide, with a mixture of hydrogen peroxide and oxygen gas, or with organic peroxy compounds.

15. A process according to any of Claims 1 and 9-14, characterized in that the peracid treatment of the pulp is carried out with peracetic, performic, perpropionic or caron acid or with a transition-metal activated peracetic, performic, perpropionic or caron acid or a combination of these.

16. A process according to any of Claims 1-15, characterized in that the chelating agent is used at a rate of 0.1-5 kg/metric ton of dry pulp.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 97/00106

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/10, D21C 9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CASONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9403553 A1 (THE PROCTER & GAMBLE COMPANY), 17 February 1994 (17.02.94), claim 1	1-16
	--	
X	WO 9514808 A1 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN), 1 June 1995 (01.06.95), the claims	1-16
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X	EP 0509382 A2 (W.R. GRACE & CO.-CONN.), 21 October 1992 (21.10.92)	1
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P,X	WO 9619557 A2 (BASF AKTIENGESELLSCHAFT), 27 June 1996 (27.06.96), claims 1,7	1
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

03/06/97

International application No.

PCT/FI 97/00106

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